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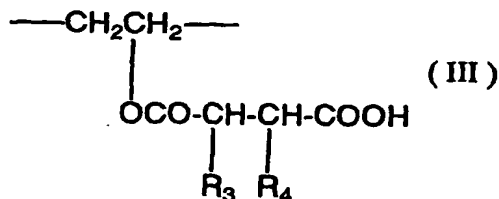
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(54) Title: THERMOSETTING POLYVINYL ALCOHOLIC BINDER RESIN COMPOSITION, SLURRY OF ELECTRODE MIX, ELECTRODE, NON-AQUEOUS ELECTROLYSIS SOLUTION-CONTAINING SECONDARY BATTERY AND THERMOSETTING POLYVINYL ALCOHOLIC BINDER RESIN AS ELECTRODE MATERIAL



(57) Abstract: The invention provides a thermosetting binder resin composition comprising: (A) a thermosetting polyvinyl alcoholic binder resin, (B) an acrylic resin plasticizer and (C) a solvent; a thermosetting binder resin composition comprising a thermosetting polyvinyl alcoholic binder resin having thermosetting units represented by general formula (III) and a solvent; a slurry of an electrode mix containing the binder resin composition; and an electrode and non-aqueous electrolysis solution-containing secondary battery using the same: wherein one of R<sub>3</sub> and R<sub>4</sub> represents a hydrogen atom and the other represents an alkenyl group. The polyvinyl alcoholic thermosetting binder resin composition is excellent in the

electrolysis solution resistance at a high temperature (50 °C) in the proximity to the upper limit of the working temperature of the lithium secondary battery, never causes any cracking, peeling out and dropping out of the electrode mix layer during the process for producing such a cell and has excellent softness and flexibility. A non-aqueous electrolysis solution-containing secondary battery assembled using electrodes each prepared by applying a slurry of an electrode mix, which comprises the thermosetting binder resin composition and a positive or negative electrode-active material, onto a current collector and then drying the coated current collector has an energy capacity whose reduction in charge-discharge cycles at 50 °C is considerably retarded and thus has an improved high temperature service life.



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## DESCRIPTION

Thermosetting Polyvinyl Alcoholic Binder Resin Composition, Slurry of  
Electrode Mix, Electrode, Non-Aqueous Electrolysis Solution-Containing  
5 Secondary battery and Thermosetting Polyvinyl Alcoholic Binder Resin as  
Electrode Material

### Technical Field

The present invention relates to a thermosetting polyvinyl alcoholic  
10 binder resin composition, a slurry of an electrode mix, an electrode, a non-  
aqueous electrolysis solution-containing secondary battery and a  
thermosetting polyvinyl alcoholic binder resin as an electrode material.

### Background Art

15 Electronic machinery and tools have gradually been miniaturized and  
have been made portable and accordingly, there has been desired for the  
development of a secondary battery, as a power supply source therefor,  
having a high energy density and an extended service life.

Recently, there has been developed a non-aqueous electrolysis  
20 solution-containing lithium ion secondary battery (hereunder referred to as  
"a lithium secondary battery"), which permits the considerable improvement  
in the energy density and such a lithium secondary battery has rapidly been  
popularized.

This lithium secondary battery principally uses a lithium-containing  
25 metal compound oxide as a positive electrode-active material and a  
carbonaceous material having a multi-layer structure, as a negative

electrode-active material, which permits the insertion of lithium ions into interstices between layers (the formation of a lithium-containing intercalation compound) and the release of lithium ions. Such a positive or negative electrode plate has been produced by kneading the corresponding active material and a binder resin composition (comprising a binder resin and a solvent such as N-methyl-2-pyrrolidone or water) to thus form a slurry of an electrode mix, applying the resulting slurry onto the both sides of a metal foil serving as a current collector, removing the solvent through the drying of the applied slurry layer to thus form a layer of the electrode mix and then subjecting the resulting product to compression molding using a roller press machine.

Polyvinylidene fluoride (hereunder referred to as "PVDF") has widely been used as such a binder resin for the both positive and negative electrodes.

However, the adherence at the boundary between the current collector and the layer of the electrode mix is insufficient when PVDF is used as a binder resin and therefore, problems arises, for instance, (1) the layer of the electrode mix is partially or completely peeled off and/or dropped out from the current collector in the process for cutting the positive and negative electrode plates or in the process for winding the electrode plates through a separator into a spiral form and (2) the layer of the electrode mix is partially or completely peeled off and/or dropped out from the current collector because of the expansion and shrinkage of the carbonaceous material as a negative electrode-active material associated with the charge-discharge cycle of the resulting lithium secondary battery and this becomes a cause of the reduction of the energy capacity in the charge-discharge cycle of the lithium

secondary battery.

As an example of means for solving these problems, Japanese Un-  
Examined Patent Publication (hereunder referred to as "J.P. KOKAI") No.  
Hei 6-172452 discloses the use of a vinylidene fluoride copolymer prepared  
5 by copolymerizing vinylidene fluoride as a principal component with a small  
amount of an unsaturated dibasic acid monoester. When using such a  
vinylidene fluoride copolymer as a binder resin, the adherence at the  
boundary between the current collector and the layer of the electrode mix is  
considerably improved, but this method is attended by various ill effects, for  
10 instance, (1) the crystallinity of the binder resin is reduced, this leads to the  
reduction of the resistance of the resin to an electrolysis solution (hereunder  
referred to as "electrolysis solution resistance") injected after the winding of  
the electrode plates, the electrode plates are in turn liable to get swollen, this  
further results in the incomplete contact between the current collector and  
15 the layer of the electrode mix at the boundary and the contact between the  
active materials in the layer of the electrode mix, this correspondingly leads  
to the destroy of the conductive network over the whole electrode plates and  
the energy capacity of the resulting cell is thus reduced and (2) the electrode  
assembly is liable to cause decomposition accompanied by the release or  
20 formation of strongly corrosive hydrogen fluoride under a high voltage  
condition, this in turn leads to an increase in the internal pressure and the  
resulting cell would fail to function. In short, the foregoing problems have  
never substantially been solved.

Moreover, as a substitute for the fluorine atom-containing system such  
25 as PVDF serving as the binder resin, there has been proposed the use of a  
diene-type synthetic rubber such as styrene-butadiene rubber (hereunder

referred to as "SBR") in J.P. KOKAI No. Hei 5-74461. Most of such diene-type synthetic rubber materials such as SBR are excellent in the electrolysis solution resistance in themselves, but the active material is substantially unstable in the slurry of the electrode mix prepared using the synthetic  
5 rubber and the active material is apt to easily undergo precipitation or sedimentation. For this reason, an additive, for instance, a thickening agent such as cellulose or a surfactant should be incorporated into the slurry. However, this results in the reduction of the energy capacity of the resulting lithium secondary battery since these additives are dissolved in the  
10 electrolysis solution used.

On the other hand, there have also been proposed various binder materials having characteristic properties different from those observed for the foregoing fluorine atom-containing or rubber-type binder resins. For instance, J.P. KOKAI Nos. Hei 9-115506, Hei 11-67215, Hei 11-67216 and  
15 Hei 11-250915 disclose binder resins capable of forming hydrogen bonds and mainly comprising polyvinyl alcohol.

However, all of these polyvinyl alcohol-based binder resins are thermoplastic materials. Accordingly, they are insufficient in the electrolysis solution resistance at a high temperature (50°C) in the proximity to the  
20 upper limit of the working temperature of the lithium secondary battery and the resulting lithium secondary battery has a short service life at a high temperature. Moreover, these resins are crystalline and hard polymers and they are insufficient in softness and flexibility. Therefore, when they are used alone, they suffer from a variety of problems such that they cause  
25 cracking, peeling off and/or dropping out of the layer of the electrode mix during the roller press-molding or winding process and it is thus difficult to

produce any normal lithium secondary battery.

#### Disclosure of the Invention

Accordingly, it is an object of the present invention to provide a  
5 polyvinyl alcoholic thermosetting binder resin composition, which is  
excellent in the electrolysis solution resistance at a high temperature (50°C)  
in the proximity to the upper limit of the working temperature of the lithium  
secondary battery, which can be used in the preparation of a cell without  
causing any cracking, peeling off and/or dropping out of a layer of an  
10 electrode mix containing the same and which is excellent in the softness and  
flexibility.

Another object of the present invention is to provide a slurry of an  
electrode mix at least comprising the foregoing polyvinyl alcoholic  
thermosetting binder resin composition and a positive or negative electrode-  
15 active material.

A still another object of the present invention is to provide an electrode  
prepared by applying the foregoing slurry of the electrode mix onto a current  
collector and then drying the coated slurry.

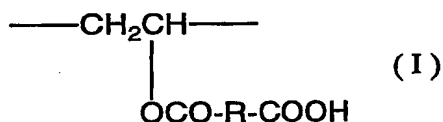
A further object of the present invention is to provide a non-aqueous  
20 electrolysis solution-containing secondary battery, which makes use of the  
foregoing electrodes, which permits substantial reduction of the energy  
capacity decrease possibly observed during charge-discharge cycles at 50°C  
and which thus has a long high temperature service life.

A still further object of the present invention is to provide a  
25 thermosetting polyvinyl alcoholic binder resin used as an electrode material  
for non-aqueous electrode-containing secondary batteries.

According to the present invention, there is thus provided a thermosetting polyvinyl alcoholic binder resin composition, a slurry of an electrode mix, an electrode, a non-aqueous electrolysis solution-containing secondary battery and a thermosetting polyvinyl alcoholic binder resin used  
 5 as an electrode material for non-aqueous electrode-containing secondary batteries, as will be detailed below.

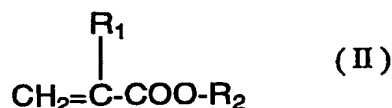
1. A thermosetting binder resin composition which comprises (A) a thermosetting polyvinyl alcoholic binder resin, (B) an acrylic resin plasticizer and (C) a solvent.

10 2. The thermosetting binder resin composition as set forth in the foregoing item 1, wherein the component (A) has thermosetting units represented by the following general formula (I):



wherein R represents a divalent organic group.

3. The thermosetting binder resin composition as set forth in the  
 15 foregoing item 1, wherein the component (B) is a polymerized product derived from a monomer represented by the following general formula (II) or a derivative thereof:



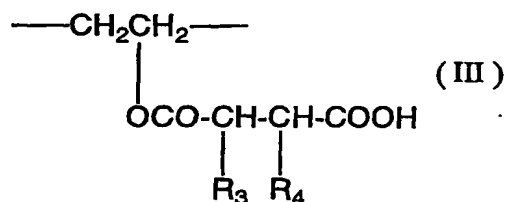
wherein R<sub>1</sub> represents a hydrogen atom or a methyl group and R<sub>2</sub> represents a hydrogen atom, a glycidyl group or an alkyl group having 6 to 18 carbon  
 20 atoms.

4. The thermosetting binder resin composition as set forth in any one of the foregoing items 1 to 3, wherein the component (C) is a nitrogen atom-



containing organic solvent or a mixed solvent containing the same.

5. A thermosetting binder resin composition which comprises a thermosetting polyvinyl alcoholic binder resin having thermosetting units represented by the following general formula (III):



5 wherein one of  $\text{R}_3$  and  $\text{R}_4$  represents a hydrogen atom and the other represents an alkenyl group and a solvent.

6. The thermosetting binder resin composition as set forth in the foregoing item 5, wherein the alkenyl group in the thermosetting unit is a dodecenyl group.

10 7. A thermosetting binder resin composition which comprises a thermosetting binder resin whose solubility parameter ranges from 24.5 to 26.5  $(\text{MJ}/\text{m}^3)^{1/2}$  and a solvent.

8. A slurry of an electrode mix which comprises a thermosetting binder resin composition as set forth in any one of the foregoing items 1 to 7 and a  
15 positive or negative electrode-active material.

9. The slurry of an electrode mix as set forth in the foregoing item 8, wherein the positive electrode-active material is a lithium-containing metal compound oxide capable of reversibly inserting and releasing lithium ions by the charge-discharge cycle.

20 10. The slurry of an electrode mix as set forth in the foregoing item 8, wherein the negative electrode-active material is a carbonaceous material capable of reversibly inserting and releasing lithium ions by the charge-

discharge cycle.

11. An electrode prepared by applying a slurry of an electrode mix as set forth in any one of the foregoing items 8 to 10 onto a current collector and then drying the coated layer of the slurry.

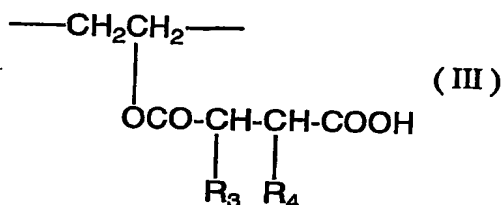
5 12. A non-aqueous electrolysis solution-containing secondary battery which comprises the electrode as set forth in the foregoing item 11.

13. A non-aqueous electrolysis solution-containing secondary battery which comprises electrodes and an electrolysis solution containing a chain organic solvent, wherein the electrode is one prepared by applying a slurry of  
10 an electrode mix, which comprises a thermosetting binder resin composition and a positive or negative electrode-active material, onto a current collector and then drying the coated slurry and wherein the difference between the solubility parameter (SP value) of the thermosetting binder resin and the SP value of the chain organic solvent is not less than  $3 \text{ (MJ/m}^3)^{1/2}$ .

15 14. The non-aqueous electrolysis solution-containing secondary battery as set forth in the foregoing item 13, wherein the degree of swelling, as determined at 50°C, of the thermosetting binder resin with respect to the electrolysis solution is not smaller than that as determined at 25°C and the former is less than 10%.

20 15. The non-aqueous electrolysis solution-containing secondary battery as set forth in the foregoing item 13, wherein the thermosetting binder resin has a winding ability.

16. The non-aqueous electrolysis solution-containing secondary battery as set forth in the foregoing item 13, wherein the thermosetting binder resin  
25 is a thermosetting polyvinyl alcoholic binder resin having thermosetting units represented by the following general formula (III):

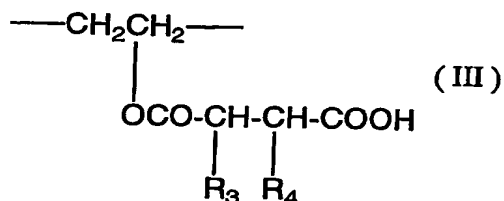


wherein one of  $\text{R}_3$  and  $\text{R}_4$  represents a hydrogen atom and the other represents an alkenyl group.

17. The non-aqueous electrolysis solution-containing secondary battery  
 5 as set forth in the foregoing item 16, wherein the alkenyl group in the thermosetting unit is a dodecenyl group.

18. The non-aqueous electrolysis solution-containing secondary battery  
 as set forth in the foregoing item 13, wherein the thermosetting binder resin composition comprises (A) a thermosetting polyvinyl alcoholic binder resin,  
 10 (B) an acrylic resin plasticizer and (C) a solvent.

19. A thermosetting polyvinyl alcoholic binder resin used as an electrode material for non-aqueous electrolysis solution-containing secondary batteries, which comprises thermosetting units represented by the following general formula (III):

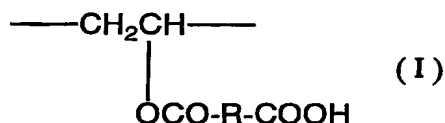


15 wherein one of  $\text{R}_3$  and  $\text{R}_4$  represents a hydrogen atom and the other represents an alkenyl group.

20. The thermosetting polyvinyl alcoholic binder resin as set forth in the foregoing item 19, wherein the alkenyl group present in the thermosetting unit is a dodecenyl group.

### Best Mode for Carrying Out the Invention

In the thermosetting binder resin composition of the present invention, the component (A) or the thermosetting polyvinyl alcoholic binder resin can be prepared by incorporating thermosetting units into a polyvinyl alcoholic resin. Examples thereof include polyvinyl alcoholic resins having introduced therein thermosetting units such as carboxyl or epoxy groups. Among these resins, polyvinyl alcoholic resins carrying carboxyl groups introduced therein are preferably used herein since they can satisfy both requirements for thermosetting property and storage stability at the same time, with polyvinyl alcoholic resins carrying thermosetting units represented by the following general formula (I) being more preferably used because of, for instance, the easiness of the introduction of carboxyl groups into the same:



wherein R represents a divalent organic group. These components (A) are preferably used alone or in any combination of at least two of them.

The thermosetting units represented by Formula (I) can in general be introduced into polyvinyl alcoholic resins through a reaction of polyvinyl alcoholic resins with a cyclic acid anhydride. In this respect, the use of an alkenyl succinic acid anhydride as such a cyclic acid anhydride permits the preparation of the thermosetting polyvinyl alcoholic binder resin having thermosetting units represented by Formula (III). The term "cyclic acid anhydride" used herein includes "alkenyl succinic acid anhydride" as well, unless otherwise specified.

The polyvinyl alcoholic resins are not restricted to specific ones, but preferably used herein from the viewpoint of, for instance, electrolysis solution resistance are those having a degree of saponification (determined according to the method for testing polyvinyl alcohol as specified in JIS K6726) of preferably not less than 85 mole%, more preferably not less than 90 mole%, particularly preferably not less than 95 mole% and most preferably not less than 98 mole%.

Moreover, the average degree of polymerization (determined according to the method for testing polyvinyl alcohol as specified in JIS K6726) of the resin preferably ranges from 500 to 5000, more preferably 1000 to 3000 and particularly preferably 1500 to 2500. This is because if the average degree of polymerization is less than 500, the active material present in the slurry of the electrode mix is liable to easily undergo sedimentation and the slurry is thus insufficient in the storage stability, while if it exceeds 5000, the resin has such a tendency that the solubility thereof in a solvent is reduced and that this makes the handling thereof difficult.

Incidentally, the foregoing polyvinyl alcoholic resin may be a variety of modified derivatives thereof (for instance, those obtained by partially introducing long chain alkyl groups into side chains thereof). These polyvinyl alcoholic resins may be used alone or in any combination of at least two of them.

The foregoing cyclic acid anhydride is not restricted to any particular one, but specific examples thereof include tetrahydrophthalic acid anhydride, methyl tetrahydrophthalic acid anhydride, trialkyl tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, methyl hexahydrophthalic acid anhydride, nadic acid anhydride, methyl nadic acid anhydride, methyl

2-substituted butenyl tetrahydrophthalic acid anhydride, itaconic acid anhydride, succinic acid anhydride, citraconic acid anhydride, dodecenyl succinic acid anhydride, maleic acid anhydride, methyl cyclopentadiene-maleic acid anhydride adduct, alkylated endoalkylene tetrahydrophthalic acid anhydride, phthalic acid anhydride, chlorendic acid anhydride, tetrachlorophthalic acid anhydride, tetrabromophthalic acid anhydride, tricarballic acid anhydride, maleic acid anhydride-linolenic acid adduct, maleic acid anhydride-sorbic acid adduct and trimellitic acid anhydride. Among these, preferred is succinic acid anhydride having low steric hindrance, from the viewpoint of, for instance, reactivity with alcoholic hydroxyl groups present in the polyvinyl alcoholic resins and the thermosetting property of the resulting component (A). These cyclic acid anhydrides are used alone or in any combination of at least two of them.

The alkenyl succinic acid anhydride used for preparing the thermosetting polyvinyl alcoholic binder resins carrying thermosetting units represented by the general formula (III) is not restricted to any particular one, but preferably used herein are those carrying dodecenyl group (an alkenyl group having 12 carbon atoms) from the viewpoint of the softness and flexibility of the resulting binder resin. These alkenyl succinic acid anhydrides are used alone or in any combination of at least two of them. In addition, cyclic acid anhydrides other than the alkenyl succinic acid anhydride may simultaneously be used for the purpose of controlling, for instance, the thermosetting property and crystallinity of the resulting binder resin.

25

In the foregoing reaction, the rate of the cyclic acid anhydride other

than the alkenyl succinic acid anhydride relative to the polyvinyl alcoholic resin preferably ranges from 0.01 to 0.50 equivalent, as expressed in terms of the amount of the acid anhydride groups of the cyclic acid anhydride, more preferably 0.03 to 0.30 equivalent and particularly preferably 0.05 to 0.20 equivalent per one equivalent of alcoholic hydroxyl groups of the polyvinyl alcoholic resin. If the amount of the acid anhydride groups of the cyclic acid anhydride is less than 0.01 equivalent, there would be observed such a tendency that the thermosetting property of the resulting component (A) is reduced and that the electrolysis solution resistance thereof is likewise reduced. On the other hand, if it exceeds 0.50 equivalent, the crosslinking density achieved after the thermosetting is too high, the resulting thermoset product is accordingly fragile, the layer of the electrode mix undergoes cracking, peeling off and dropping out during the cell-manufacture steps and it is thus quite difficult to prepare a normal cell. In addition, the resulting product is liable to include un-reacted cyclic acid anhydride.

The rate of the alkenyl succinic acid anhydride (+ other cyclic acid anhydrides) relative to the polyvinyl alcoholic resin is not particularly restricted, but the amount of the acid anhydride groups of the alkenyl succinic acid anhydride (+ other cyclic acid anhydrides) preferably ranges from 0.001 to 0.50 equivalent, more preferably 0.005 to 0.30 equivalent and particularly preferably 0.01 to 0.20 equivalent per one equivalent of the alcoholic hydroxyl groups of the polyvinyl alcoholic resin. If the amount of the acid anhydride groups of the alkenyl succinic acid anhydride (+ other cyclic acid anhydrides) is less than 0.001 equivalent, there are observed such a tendency that the softness and flexibility of the resulting product are liable to be insufficient, that the thermosetting property thereof is also reduced

and that the electrolysis solution resistance thereof is likewise reduced. On the other hand, if it exceeds 0.50 equivalent, the crosslinking density achieved after the thermosetting is too high, the resulting thermoset product is accordingly fragile, the layer of the electrode mix undergoes cracking,  
5 peeling off and dropping out during the cell-manufacture steps and it is thus quite difficult to prepare a normal cell. In addition, there is also observed such a tendency that the crystallinity thereof is reduced, that the electrolysis solution resistance of the product is lowered and that the resulting product contains un-reacted alkenyl succinic acid anhydride (+ other cyclic acid  
10 anhydrides).

The foregoing reaction of the polyvinyl alcoholic resin with the cyclic acid anhydride is preferably carried out in an organic solvent under substantially moisture free conditions. The organic solvent used herein is not  
15 particularly restricted and specific examples thereof include amides such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide and N,N-dimethylformamide; ureas such as N,N-dimethyl-ethylene urea, N,N-dimethyl-propylene urea and tetramethyl urea; lactones such as  $\gamma$ -butyrolactone and  $\gamma$ -caprolactone; carbonates such as propylene carbonate; ketones  
20 such as methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; esters such as ethyl acetate, n-butyl acetate, butyl cellosolve acetate, butyl carbitol acetate, ethyl cellosolve acetate and ethyl carbitol acetate; glymes such as diglyme, triglyme and tetraglyme; hydrocarbons such as toluene, xylene and cyclohexane; and sulfones such as sulfolane. Among these,  
25 preferred are nitrogen atom-containing organic solvents such as amides and ureas because of, for instance, the high solubility in the polyvinyl alcoholic



resins and the high ability of accelerating the reaction of the polyvinyl alcoholic resin with the cyclic acid anhydride. Examples thereof more preferably used include N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethyl-ethylene urea, N,N-dimethyl-propylene urea and tetramethyl urea since they are, for instance, free of any active hydrogen, which is liable to inhibit the reaction of the polyvinyl alcoholic resin with the cyclic acid anhydride, with the use of N-methyl-2-pyrrolidone being particularly preferred. These organic solvents may be used alone or in any combination of at least two of them.

10       The amount of the organic solvent to be used preferably ranges from 50 to 10,000 parts by mass, more preferably 200 to 5,000 parts by mass and particularly preferably 300 to 3,000 parts by mass per 100 parts by mass of the sum of the polyvinyl alcoholic resin and the cyclic acid anhydride. If the amount thereof used is less than 50 parts by mass, their solubilizing ability is insufficient and this in turn makes the reaction system heterogeneous and highly viscous, while if it exceeds 10,000 parts by mass, the reaction is not easily completed.

20       The reaction of the polyvinyl alcoholic resin with the cyclic acid anhydride is carried out at a temperature preferably ranging from 40 to 250°C, more preferably 60 to 200°C and particularly preferably 80 to 150°C. In addition, the reaction time is preferably not less than 10 minutes, more preferably 30 minutes to 10 hours and particularly preferably 1 to 5 hours. If the reaction temperature is lower than 40°C, the reaction does not proceed easily and it is difficult to complete the reaction. On the other hand, if it exceeds 250°C, the reaction system may sometimes undergo gelation because of side reactions and this makes the control of the reaction difficult. If the

reaction time is less than 10 minutes, it is difficult to complete the reaction.

In the reaction of the polyvinyl alcoholic resin with the cyclic acid anhydride, a catalyst may, if necessary, be used. Examples of such catalysts are tertiary amines such as triethylamine, triethylenediamine, N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethylbenzylamine, N-methylmorpholine, N-ethylmorpholine, N,N-dimethyl-piperazine, pyridine, picoline and 1,8-diazabicyclo[5,4,0]undecene-7; imidazoles such as 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-methyl-4-methyl-imidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-phenylimidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole and 1-azine-2-methylimidazole; organic tin compounds such as dibutyl-tin dilaurate and 1,3-diacetoxy tetrabutyl distannoxane; quaternary onium salts such as tetraethyl-ammonium bromide, tetrabutyl-ammonium bromide, benzyltriethyl- ammonium chloride, trioctylmethyl-ammonium chloride, cetyltrimethyl-ammonium bromide, tetrabutyl-ammonium iodide, dodecyltrimethyl-ammonium iodide, benzyldimethyl tetradecyl-ammonium acetate, tetraphenyl-phosphonium chloride, triphenylmethyl-phosphonium chloride and tetramethyl-phosphonium bromide; organic phosphorus compounds such as 3-methyl-1-phenyl-2-phosphorene-1-oxide; alkali metal salts of organic acids such as sodium benzoate and potassium benzoate; inorganic salts such as zinc chloride, iron chloride, lithium chloride and lithium bromide; metal carbonyl compounds such as octacarbonyl dicobalt (II) (cobalt carbonyl); and metal ether compounds such as tetrabutoxy titanium. These catalysts may be used alone or in any combination of at least two of them. The amount of these

catalysts used ranges from about 0.01 to 10% by mass on the basis of the solid contents of the reaction system.

The solubility parameter of the thermosetting polyvinyl alcoholic binder resin of the present invention preferably ranges from 23.5 to 27.5 (MJ/m<sup>3</sup>)<sup>1/2</sup>, and more preferably 24.5 to 26.5 (MJ/m<sup>3</sup>)<sup>1/2</sup>.

The acrylic resin plasticizers as the component (B) used in the present invention are not restricted to specific ones inasmuch as they can impart winding properties to electrodes and examples thereof preferably include polymers of monomers represented by the following general formula (II) or derivatives thereof:



wherein R<sub>1</sub> represents a hydrogen atom or a methyl group and R<sub>2</sub> represents a hydrogen atom, a glycidyl group or an alkyl group having 6 to 18 carbon atoms). More preferably used herein are copolymers of monomers represented by Formula (II) wherein R<sub>2</sub> represents an alkyl group having 6 to 18 carbon atoms with monomers represented by Formula (II) wherein R<sub>2</sub> represents a hydrogen atom or a glycidyl group or derivatives of these copolymers and particularly preferably used herein are derivatives of copolymers prepared by copolymerizing monomers represented by Formula (II) wherein R<sub>1</sub> represents a hydrogen atom and R<sub>2</sub> represents an alkyl group having 12 carbon atoms (lauryl acrylate) with monomers represented by Formula (II) wherein R<sub>1</sub> represents a hydrogen atom and R<sub>2</sub> represents a hydrogen atom (acrylic acid). In this respect, if the carbon atom number of the alkyl group represented by R<sub>2</sub> is less than 6, the electrolysis solution resistance of the resulting resin plasticizer is reduced. On the other hand, if

the carbon atom number thereof exceeds 18, the polymerizability of the monomers is reduced. These components (B) may be used alone or in any combination of at least two of them.

If using the lauryl acrylate-acrylic acid copolymer as a precursor for the component (B), the weight average molecular weight thereof preferably ranges from 1,000 to 1,000,000, more preferably 1,000 to 100,000 and particularly preferably 1,000 to 10,000. This is because if the weight average molecular weight thereof is less than 1,000, the resulting plasticizer may not show its desired function, while if it exceeds 1,000,000, the compatibility of the plasticizer with the component (A) and the solubility thereof in the solvent are reduced and this in turn makes the handling thereof difficult.

Moreover, the acid value of the copolymer preferably ranges from 10 to 500 KOH mg/g, more preferably 30 to 200 KOH mg/g and particularly preferably 50 to 150 KOH mg/g. If the acid value thereof is less than 10 KOH mg/g, it is difficult to obtain any derivative thereof, while if it exceeds 500 KOH mg/g, the resulting derivative has insufficient function as the plasticizer.

When using a derivative of a lauryl acrylate-acrylic acid copolymer as the component (B), examples of such derivatives include reaction products of lauryl acrylate-acrylic acid copolymers with, for instance, polyoxazoline, polyisocyanate, melamine resin, polycarbodiimide, polyol, polyamine and epoxy resin. Among these derivatives, preferred are reaction products of lauryl acrylate-acrylic acid copolymers with epoxy resins, since they can easily be prepared, have good compatibility with the component (A) and have a high ability to impart a high plasticizing ability to the thermosetting binder resin composition of the present invention.

Examples of the foregoing epoxy resins are bifunctional aromatic glycidyl ethers such as bisphenol A type epoxy resins, tetrabromo-bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol AD type epoxy resins, naphthalene type epoxy resins, biphenyl type epoxy resins and  
5 tetramethyl-biphenyl type epoxy resins; polyfunctional aromatic glycidyl ethers such as phenol-novolak type epoxy resins, cresol-novolak type epoxy resins, dicyclopentadiene-phenol type epoxy resins and tetraphenylol-ethane type epoxy resins; bifunctional aliphatic glycidyl ethers such as polyethylene glycol type epoxy resins, polypropylene glycol type epoxy resins, neopentyl  
10 glycol type epoxy resins, dibromo-neopentyl glycol type epoxy resins and hexanediol type epoxy resins; bifunctional alicyclic glycidyl ethers such as hydrogenated bisphenol A type epoxy resins; polyfunctional aliphatic glycidyl ethers such as trimethylolpropane type epoxy resins, sorbitol type epoxy resins and glycerin type epoxy resins; bifunctional aromatic glycidyl esters  
15 such as diglycidyl phthalate; bifunctional alicyclic glycidyl esters such as diglycidyl esters of tetrahydro-phthalic acid, diglycidyl esters of hexahydro-phthalic acid, diglycidyl esters of dimeric acids and diglycidyl esters of hydrogenated dimeric acids; bifunctional aromatic glycidyl-amines such as N,N-diglycidyl-aniline and N,N-diglycidyl-trifluoromethyl-aniline;  
20 polyfunctional aromatic glycidyl-amines such as N,N,N',N'-tetraglycidyl-4,4-diaminodiphenyl methane, 1,3-bis(N,N-glycidylaminomethyl)cyclohexane and N,N,O-triglycidyl-p-aminophenol; bifunctional alicyclic epoxy resins such as alicyclic diepoxyacetal, alicyclic diepoxy-adipate, alicyclic diepoxy-carboxylate and vinylcyclohexene dioxide; bifunctional heterocyclic epoxy  
25 resins such as diglycidyl hydantoin; polyfunctional heterocyclic epoxy resins such as triglycidyl isocyanurate; bifunctional or polyfunctional silicon

containing epoxy resins such as organo-polysiloxane type epoxy resins; and epoxy resins prepared by chain-extension reactions of the foregoing bifunctional epoxy resins with aliphatic dicarboxylic acids (such as succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, 5 dodecane-dicarboxylic acid, eicosane-dicarboxylic acid, alkylene ether bond-containing dicarboxylic acids, alkylene carbonate bond-containing dicarboxylic acids, butadiene bond-containing dicarboxylic acids, hydrogenated butadiene bond-containing dicarboxylic acids and dimethylsiloxane bond-containing dicarboxylic acids) and/or alicyclic dicarboxylic 10 acids (such as 1,4-cyclohexane dicarboxylic acids, dimeric acids and hydrogenated dimeric acids).

Among these, preferably used herein are bifunctional epoxy resins from the viewpoint of simultaneous achievement of the plasticity and thermosetting property of the polyvinyl alcohol thermosetting binder resin 15 composition of the present invention. These epoxy resins may be used alone or in any combination of at least two thereof.

In the reaction (derivatization), the amount of the epoxy resins relative to the lauryl acrylate-acrylic acid copolymer preferably ranges from 0.01 to 5 equivalent, more preferably 0.1 to 4 equivalent, particularly 20 preferably 0.3 to 3 equivalent and most preferably 0.5 to 2 equivalent as expressed in terms of the amount of the epoxy groups of the former per one equivalent of the carboxyl groups of the latter. If the quantity of the epoxy groups of the epoxy resin is less than 0.01 equivalent, the compatibility thereof with the component (A) is insufficient and the resulting polyvinyl 25 alcoholic thermosetting binder resin composition of the present invention has insufficient plasticity, while if it exceeds 5 equivalents, the degree of

crosslinking thereof becomes too high due to side reactions and therefore, the reaction system is liable to undergo gelation.

The temperature of the reaction of a lauryl acrylate-acrylic acid copolymer with an epoxy resin preferably ranges from 40 to 250°C, more preferably 60 to 200°C and particularly preferably 80 to 150°C. In addition, the time required for the reaction is preferably not less than 10 minutes, more preferably 30 minutes to 10 hours and particularly preferably 1 to 5 hours. If the reaction temperature is less than 40°C, it is difficult to complete the reaction, while if it exceeds 250°C, the reaction system sometimes undergoes gelation due to side reactions and this would make the control of the reaction difficult. In addition, if the reaction time is less than 10 minutes, it is difficult to complete the reaction.

The component (C) used in the present invention is not restricted to any particular one, but specific examples thereof are water and alcohols as well as the foregoing organic solvents listed above in connection with and usable in the reactions of the polyvinyl alcoholic resins with the cyclic acid anhydrides. Among these, preferably used herein are nitrogen atom-containing organic solvents such as amides and ureas, with N-methyl-2-pyrrolidone or mixed solvents containing the same being more preferred among others. The component (C) may be used alone or in any combination of at least two thereof.

The amount of the component (B) relative to the component (A) in the thermosetting binder resin composition of the present invention preferably ranges from 1 to 50 parts by mass, more preferably 3 to 30 parts by mass and

particularly preferably 5 to 20 parts by mass per 100 parts by mass of the component (A). If the amount of the component (B) is less than one part by mass, the plasticity attained is insufficient, while if it exceeds 50 parts by mass, the thermosetting property of the resulting composition is reduced and  
5 this accordingly results in the reduction of the electrolysis solution resistance. The amount of the component (C) to be incorporated into the composition of the present invention should be any amount such that the concentration thereof is not too low since the component (C) is, if necessary, supplemented during the subsequent step for preparing a slurry of an  
10 electrode mix.

The thermosetting binder resin composition containing a thermosetting polyvinyl alcoholic binder resin carrying thermosetting units represented by Formula (III) can impart a winding ability to the resulting electrodes containing the same even if any component (B) is not used.

15 The thermosetting binder resin composition of the present invention may, if necessary, comprise, in addition to the foregoing components (A), (B) and (C), a variety of additives such as thixotropic properties-imparting agents, thickening agents and dispersants for preventing any sedimentation  
20 of the active material present in the slurry of the electrode mix, anti-foaming agents for the improvement of the electrode-coating properties and leveling agents.

A first slurry of an electrode mix according to the present invention  
25 comprises at least a thermosetting binder resin composition containing the foregoing components (A), (B) and (C) and a positive electrode-active



material or a negative electrode-active material.

In addition, a second slurry of an electrode mix according to the present invention comprises at least a thermosetting binder resin composition which comprises a thermosetting polyvinyl alcoholic binder resin having thermosetting units represented by Formula (III) and a solvent, and a positive electrode-active material or a negative electrode-active material. The foregoing solvent is not particularly restricted, but examples thereof include water and alcohols as well as organic solvents listed above in connection with and usable in the reaction with the alkenyl succinic acid anhydride (+ other cyclic acid anhydride). Among these, preferably used herein are nitrogen containing organic solvents such as amides and ureas, with N-methyl-2-pyrrolidone or mixed solvents containing the same being more preferred among others. These solvents may be used alone or in any combination of at least two thereof.

The foregoing positive and negative electrode-active materials are not restricted to specific ones inasmuch as they can reversibly insert and/or release lithium ions through the charge-discharge cycle of the lithium secondary battery.

Examples of such positive electrode-active materials are preferably lithium-containing metal compound oxides comprising lithium and at least one metal selected from the group consisting of iron, cobalt, nickel and manganese. On the other hand, examples of such negative electrode-active materials are preferably carbonaceous materials such as amorphous carbon, graphite, carbon fibers, coke and active carbon and it is also possible to use composite materials comprising such carbonaceous materials and metals

such as silicon, tin and silver or oxides thereof. These active materials may be used alone or in any combination of at least two thereof.

In this connection, the slurry of an electrode mix for positive electrodes may likewise comprise at least one auxiliary conductivity-  
5 imparting agent selected from the group consisting of, for instance, carbon black and acetylene black.

The volume ratio [binder resin/active material] of the thermosetting polyvinyl alcoholic binder resin to the positive or negative electrode-active material present in the slurry of the electrode mix preferably ranges from  
10 [1/99] to [20/80]. If the volume ratio [binder resin/active material] is less than [1/99], the resulting layer of the electrode mix would undergo cracking, peeling off and/or dropping out from the current collector during the process for preparing a cell and it is difficult to produce a normal cell, while if it exceeds [20/80], there is observed such a tendency that the energy capacity of  
15 the resulting lithium-containing secondary battery is reduced. In this respect, the rate of the solvent to be incorporated into the slurry may be arbitrarily selected, but should be such that the slurry is not excessively diluted therewith.

20 The electrodes of the present invention can be produced by applying the foregoing slurry of the electrode mix onto a current collector and then drying the coated layer and the non-aqueous electrolysis solution-containing secondary battery of the present invention is prepared using such electrodes. The methods for preparing the electrodes and non-aqueous electrolysis  
25 solution-containing secondary battery of the present invention are not restricted to specific ones and they can be prepared according to any known

methods, respectively.

The non-aqueous electrolysis solution used in the non-aqueous electrolysis solution-containing secondary battery of the present invention is not restricted to specific ones inasmuch as they can ensure the function of the resulting cell as a secondary battery. Specific examples thereof are solutions obtained by dissolving electrolysis solutions such as  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiI}$ ,  $\text{LiCl}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiCF}_3\text{CO}_2$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiB}_{10}\text{Cl}_{10}$ ,  $\text{LiAlCl}_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiB}(\text{C}_2\text{H}_5)_4$ ,  $\text{LiCH}_3\text{SO}_3$ ,  $\text{LiC}_4\text{F}_9\text{SO}_3$  and/or  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  in organic solvents, for instance, carbonates such as propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate and methyl ethyl carbonate; lactones such as  $\gamma$ -butyrolactone; ethers such as trimethoxy-methane, 1,2-dimethoxy-ethane, diethyl ether, 2-ethoxy-ethane, tetrahydrofuran and 2-methyl-tetrahydrofuran; sulfoxides such as dimethyl sulfoxide; oxolanes such as 1,3-dioxolane and 4-methyl-1,3-dioxolane; nitrogen atom-containing organic solvents such as acetonitrile, nitromethane and N-methyl-2-pyrrolidone; esters such as methyl formate, methyl acetate, butyl acetate, methyl propionate, ethyl propionate and phosphoric acid triesters; glymes such as diglyme, triglyme and tetraglyme; ketones such as acetone, diethyl ketone, methyl ethyl ketone and methyl isobutyl ketone; sulfones such as sulfolane; oxazolidinones such as 3-methyl-2-oxazolidinone; and sultones such as 1,3-propane-sultone, 4-butane-sultone and naphthasultone. Among these non-aqueous electrolysis solutions, preferred are those obtained by dissolving  $\text{LiPF}_6$  in carbonates. The foregoing organic solvents used for preparing such non-aqueous electrolysis solutions may be used alone or in any combination.

The solubility parameter (SP value) of the chain organic solvent for the non-aqueous electrolysis solution is preferably selected in such a manner that the difference between the SP values thereof and the binder resin used is not less than  $3 \text{ (MJ/m}^3)^{1/2}$ . If the difference is less than  $3 \text{ (MJ/m}^3)^{1/2}$ , the affinity of the resin for the solvent is extremely high and the resin is accordingly liable to get swollen. The SP values of dimethyl carbonate and diethyl carbonate used in Examples of the present invention as such chain organic solvents are  $20.3 \text{ (MJ/m}^3)^{1/2}$  and  $18.0 \text{ (MJ/m}^3)^{1/2}$ , respectively and that of ethylene carbonate as a cyclic solvent is  $30.1 \text{ (MJ/m}^3)^{1/2}$ .

In this respect, the SP value of each binder resin can be calculated on the basis of the chemical structure thereof (OKITSU Toshinao: "The Role of Solubility Parameter (SP) in 1DP21 Polymer Blend", Collected Resumes of The 2nd Polymer Materials Forum, 1993, pp. 167-168). Moreover, the SP values of organic solvents in electrolysis solutions are those purely thermodynamically determined (A.F.M.Barton, Chem. Rev., 1975, 75:731; MUKAI Junji & KINJO Noriyuki, "Practical Polymer Science for Engineers", Tokyo, Published by KODANSHA Publishing Company, 1981, pp. 80-85; and MIHARA Kazuyuki, "Explanatory Paint and Varnish Technology", Tokyo, Published by RIKO-SHUPPAN Publishing Company, 1971, pp. 115-116).

However, there is a considerable difference between the calculated SP value ( $14.1 \text{ (MJ/m}^3)^{1/2}$ ) of PVDF and the practically found value ( $23.2 \text{ (MJ/m}^3)^{1/2}$ ) thereof and therefore, the SP value of PVDF disclosed in the present specification is the found one.

Moreover, in the non-aqueous electrolysis solution-containing secondary battery of the present invention, the degree of swelling of the thermosetting binder resin with respect to the electrolysis solution as

determined at 50°C is desirably less than 10% and preferably less than 5%. If a thermosetting binder resin in an ideally adhered state excessively gets swollen through the absorption of an electrolysis solution, there are observed incomplete contact between active materials and/or between active materials  
5 and a current collector since the distances therebetween increase. In addition, if the adhesive force of a thermosetting binder resin in an electrolysis solution is reduced, the binder resin undergoes peeling and this results in incomplete contact in the resulting cell. For this reason, it is considered that the conductivity of the electrodes produced using the same is  
10 reduced, that the service or working time of the cell is likewise reduced because of the reduction of the capacity of the cell and that the output of the cell is reduced due to an increase of the internal resistance of the cell.

The thermosetting binder resin of the present invention desirably has  
15 a winding ability. A negative electrode (a blend of amorphous carbon having an average particle size of 20  $\mu$ m and a thermosetting polyvinyl alcoholic binder resin composition in a volume ratio (of solid contents) of 90 : 10, obtained after drying in a vacuum at 150°C for 16 hours) is cut into a piece having a size of width 60 mm  $\times$  length 20 mm in a dry room (temperature: 23  
20  $\pm$  2°C; humidity: 5  $\pm$  2%), wound on a stainless steel rod having a diameter of 4 mm  $\phi$  in such a manner that the surface on which the layer of an electrode mix is provided is exposed, the both ends thereof are put on top of each other and then a weight of 100 g is loaded onto the same. Such a condition is maintained for one minute, the surface of the electrode mix layer is inspected  
25 for the presence of any apparent defect such as cracks or wrinkles and evaluated on the basis of the following criteria: windable: there is not

observed any crack and/or wrinkle on the surface of the electrode mix layer;  
un-windable: there are observed apparent defects.

### Examples

5           The present invention will hereunder be described in more detail with  
reference to the following Examples, but the present invention is not  
restricted to these specific Examples at all.

#### Synthetic Example 1: Synthesis of Component (A)

10           To a one liter volume separable flask equipped with a stirring machine,  
a thermometer, a condenser, a distillation tube and a nitrogen gas-  
introduction tube, there were added 51.01 g of a polyvinyl alcohol (available  
from Unitika Ltd. under the trade name of Unitika Poval UF200G, the  
average degree of polymerization: 2000; the degree of saponification: 98 to 99  
15 mole%; the content of adsorbed water and others (weight loss observed after  
drying on a hot plate of 150°C for 30 minutes): 5.3% by mass), 644 g of N-  
methyl-2-pyrrolidone (hereunder referred to as "NMP") as the component (C)  
and 10 g of toluene and the temperature was raised up to 195°C by heating  
over 30 minutes in a nitrogen gas stream with stirring. Moisture present in  
20 the system began to be distilled in the form of an azeotropic mixture with  
toluene in the course of the heating and from an instance when the  
temperature exceeded about 185°C. The mixture was maintained at that  
temperature for 1 to 2 hours till all of the moisture was thus substantially  
distilled off from the system while refluxing the toluene, the toluene in the  
25 system was distilled off and then the system was cooled down to 120°C. The  
distillate (moisture and others) was found to be about 3 ml.

Then, to the dehydrated solution of the polyvinyl alcohol maintained at 120°C, there was added 7.69 g of succinic acid anhydride (0.07 equivalent as expressed in terms of the amount of the acid anhydride groups per one equivalent of the alcoholic hydroxyl groups of the polyvinyl alcohol), the mixture was maintained at that temperature for one hour to thus make the reaction proceed and then cooled down to room temperature to give a solution of the component (C) containing 8% by mass of the component (A).

The resulting component (A) was found to have a weight average molecular weight (as determined by GPC and more specifically, determined using, as an eluent, an aqueous solution prepared in such a manner that the concentration of sodium chloride as an emollient agent was 0.1 mole/l, and a calibration curve prepared using standard polyethylene oxide-polyethylene glycol, as expressed in terms of a polyethylene oxide-polyethylene glycol-reduced value) of 170,000 and an acid value of 78 KOH mg/g.

In addition, the SP value of the resulting component (A) was found to be  $25.4 \text{ (MJ/m}^3)^{1/2}$ .

#### Preparation Example 1: Preparation of Polyvinyl Alcohol Aqueous Solution

To a 0.3 liter volume separable flask equipped with a stirring machine, a thermometer and a condenser, there were added 16.90 g of a polyvinyl alcohol identical to that used in Synthetic Example 1 and 183.1 g of pure water and the temperature was raised up to 95°C over 10 minutes with stirring. After completely dissolving the polyvinyl alcohol by maintaining the mixture at that temperature for one hour, the mixture was cooled to room temperature to give a 8% by mass aqueous solution of the polyvinyl alcohol. Separately, NMP was substituted for the pure water used above to prepare

an NMP solution of the polyvinyl alcohol, but the whole system was solidified in the course of cooling the same to room temperature and therefore, such an NMP solution could not be prepared.

#### 5 Synthetic Example 2: Synthesis of Component (B)

To a 0.3 liter volume separable flask equipped with a stirring machine, a thermometer, a condenser and a nitrogen gas-introduction tube, there were added 109.29 g of a solvent-free lauryl acrylate-acrylic acid copolymer (available from SOKEN Chemical Co., Ltd. under the trade name of  
10 ACTFLOW CBL3098, weight average molecular weight: 3100; acid value: 97 KOH mg/g) and 70.71 g (2 equivalents as expressed in terms of the amount of the epoxy groups per one equivalent of the carboxyl groups of the solvent-free lauryl acrylate-acrylic acid copolymer) of a bisphenol A type epoxy resin (available from Mitsui Chemicals, Inc. under the trade name of EPOMIK  
15 R140P, epoxy equivalent: 187 g/eq.), followed by the elevation of the temperature of the mixture up to 150°C over 10 minutes in a nitrogen gas stream with stirring. After the reaction of these components at that temperature for 2 hours, 77.14 g of NMP as the component (C) was added to the reaction system and then the mixture was cooled to room temperature to  
20 thus give a solution of the component (C) containing 70% by mass of the component (B).

The resulting component (B) was found to have a weight average molecular weight (as determined by GPC and more specifically, determined using, as an eluent, tetrahydrofuran and a calibration curve prepared using  
25 standard polystyrene, as expressed in terms of a polystyrene-reduced value) of 21,000, an epoxy equivalent of 2377 g/eq and an acid value of less than 1



KOH mg/g.

The thermosetting properties and the electrolysis solution resistance of the component (A) prepared in Synthetic Example 1 were evaluated by comparing the component with the polyvinyl alcohol as the raw material.

5 The following are a method for preparing a film and methods for evaluating the thermosetting properties and the electrolysis solution resistance. The following Table 1 shows the results obtained in the evaluation of the thermosetting properties and the electrolysis solution resistance.

#### 10 Preparation of Film

After uniformly casting a predetermined solution on a polyethylene terephthalate (hereunder referred to as "PET") film in such a manner that the film thickness as determined after drying and a heat treatment was equal to about  $30\mu\text{m}$ , the cast film was dried on a hot plate maintained at  
15  $100^{\circ}\text{C}$  for one hour under ordinary pressure. Then the dried film was subjected to a heat treatment in a vacuum dryer maintained at  $150^{\circ}\text{C}$  for 3 hours under reduced pressure, the heat-treated film was peeled off from the PET film and it was further vacuum-dried at  $100^{\circ}\text{C}$  for 2 hours to thus give a film.

20

#### Method for Evaluating Thermosetting Properties

After weighing out about 30 mg of the film prepared above in a completely dried atmosphere maintained at  $25^{\circ}\text{C}$ , immersing the weighed film in about 8 ml of NMP in a 13.5 ml glass screw bottle and tightly stopping  
25 the bottle, the bottle was heated in an oil bath maintained at  $150^{\circ}\text{C}$  for 30 minutes and the thermosetting properties of the film was evaluated

according to the following criteria: Insufficient thermosetting properties: a film sample is completely dissolved; good thermosetting properties: a film sample is not dissolved in the solvent and maintains its original shape.

#### 5 Method for Evaluating Electrolysis solution Resistance

After accurately weighing out about 30 mg of the film prepared above in a completely dried atmosphere maintained at 25°C, immersing the weighed film in about 8 ml of a non-aqueous electrolysis solution (a 1M solution of lithium hexafluoro-phosphate in a 1/1/1 (volume ratio) mixed liquid of ethylene carbonate/dimethyl carbonate/diethyl carbonate, available from Kishida Chemical Co., Ltd., lithium secondary battery electrolysis solution grade, those appearing in the following description are shown in the same way) in a 13.5 ml glass screw bottle and tightly stopping the bottle, the bottle was stored in a thermostatic chamber maintained at 25°C and that maintained at 50°C over 24 hours.

Then the film were removed from the non-aqueous electrolysis solution in a completely dried atmosphere of 25°C, followed by wiping the non-aqueous electrolysis solution adhered to the film surface away with dry paper to thus determine any change of the mass. The degree of swelling due to the absorption of the non-aqueous electrolysis solution was calculated on the basis of the following equation and the electrolysis solution resistance values of these films were evaluated on the following criteria: A sample film whose degree of swelling at 50°C is smaller than that observed at 25°C is considered to be dissolved in the electrolysis solution and therefore, it is judged to be bad in the electrolysis solution resistance; a sample film whose degree of swelling at 50°C is not smaller than that observed at 25°C, but

exceeds 100% is likewise judged to be bad in the electrolysis solution resistance; a sample film whose degree of swelling at 50°C is not smaller than that observed at 25°C and falls within the range of from 10 to 100% is judged to be acceptable in the electrolysis solution resistance; and a film  
 5 sample whose degree of swelling at 50°C is not smaller than that observed at 25°C and is less than 10% is judged to be good in the electrolysis solution resistance.

Degree of Swelling (%) = [(Mass after immersion - mass before  
 10 immersion)/mass before immersion] × 100

Table 1

| Item  | Component (A)  | Raw Polyvinyl Alcohol     |
|---|--|---------------------------|
| Thermosetting Properties:<br>Dissolved condition of Film<br><br>Judgment                                      | Insoluble (the original shape is maintained)<br>Good | Completely Soluble<br>Bad |
| Electrolysis Solution Resistance:<br>Deg. of Swelling at 25°C (%)<br>Deg. of Swelling at 50°C (%)<br>Judgment | 1<br>2<br>Good                                       | 9<br>4<br>Bad             |

The foregoing results clearly indicate that the component (A) used in  
 15 the present invention has good thermosetting properties and electrolysis solution resistance, which cannot be achieved by the raw polyvinyl alcohol.

#### Example 1 (Preparation of Thermosetting Binder Resin Composition of the Invention)

20 There were admixed 100 parts by mass (as expressed in terms of the

reduced amount of the component (A)) of the solution of the component (C) containing 8% by mass of the component (A) prepared in Synthetic Example 1 with 10 parts by mass (as expressed in terms of the reduced amount of the component (B)) of the solution of the component (C) containing 70% by mass of the component (B) prepared in Synthetic Example 2 to give a thermosetting binder resin composition of the present invention.

The thermosetting binder resin composition prepared in Example 1 was inspected for the thermosetting properties and the electrolysis solution resistance while comparing them with those observed for PVDF. The results thus obtained are summarized in the following Table 2.

Table 2

| Item  | Product of the Present Invention                     | PVDF                      |
|---|--|---------------------------|
| Thermosetting Properties:<br>Dissolved condition of Film<br>Judgment  | Insoluble (the original shape is maintained)<br>Good | Completely Soluble<br>Bad |
| Electrolysis Solution Resistance:<br>Deg. of Swelling at 25°C (%)<br>Deg. of Swelling at 50°C (%)<br>Judgment | 1<br>2<br>Good                                       | 16<br>20<br>Acceptable    |

The foregoing results clearly indicate that the thermosetting plasticized polyvinyl alcoholic binder resin composition of the present invention has good thermosetting properties and electrolysis solution resistance, which cannot be achieved by PVDF.

#### Example 2 (Preparation of Slurry of Positive Electrode Mix)

There were admixed lithium-rich lithium manganese(III,IV) oxide

( $\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$ ), as a positive electrode-active material, having an average particle size of  $10\mu\text{m}$ , an auxiliary conductivity-imparting agent (artificial graphite) having an average particle size of  $3\mu\text{m}$  and the thermosetting binder resin composition prepared in Example 1 in a volume ratio of 80 : 10 : 10 (solid contents), followed by kneading the mixture while NMP was, if necessary, supplemented to prepare a slurry of positive electrode mix.

Examples 3 and 4 and Comparative Examples 1 to 6 (Preparation of Slurries of Positive Electrode Mixes)

The same procedures used in Example 2 were repeated except for using components listed in the following Table 3 to thus give corresponding slurries of positive electrode mixes having compositions specified in Table 3.

Table 3

| Ex. No. | Item  |  |
|---------|---|--|
|         | Positive Electrode-Active Material<br>(average particle size: $10\mu\text{m}$ ) | Binder Resin Composition<br>(a solution in NMP)            |
| 3       | Lithium cobalt(III) oxide<br>$\text{LiCoO}_2$                                   | The product of the present invention prepared in Example 1 |
| 4       | Lithium nickel(III) oxide<br>$\text{LiNiO}_2$                                   | The product of the present invention prepared in Example 1 |
| 1*      | Lithium-rich lithium manganese(III,IV) oxide                                    | PVDF   |
| 2*      | Lithium cobalt(III) oxide   | PVDF   |
| 3*      | Lithium nickel(III) oxide   | PVDF   |
| 4*      | Lithium-rich lithium manganese(III,IV) oxide                                    | The component (A) alone prepared in Synthetic Example 1    |
| 5*      | Lithium cobalt(III) oxide   | The component (A) alone prepared in Synthetic Example 1    |
| 6*      | Lithium nickel(III) oxide   | The component (A) alone prepared in Synthetic Example 1    |

15 \*: Comparative Example

Note 1: The auxiliary conductivity-imparting agent used in these Examples

and Comparative Examples was identical to that used in Example 2.

Note 2: The volume ratio of the positive electrode-active material, the auxiliary conductivity-imparting agent and the binder resin composition (solid contents) was also identical to that used in Example 2.

5

#### Example 5 (Preparation of Slurry of Negative Electrode Mix)

There were admixed amorphous carbon having an average particle size of  $20\mu\text{m}$  as a negative electrode-active material and the thermosetting plasticized polyvinyl alcoholic binder resin composition prepared in Example 1 in a volume ratio (of solid contents) of 90 : 10, followed by kneading the mixture while NMP was, if necessary, supplemented to prepare a slurry of negative electrode mix.

#### Example 6 and Comparative Examples 7 to 10 (Preparation of Slurries of Negative Electrode Mixes)

The same procedures used in Example 5 were repeated except for using components listed in the following Table 4 to thus give corresponding slurries of negative electrode mixes having compositions specified in Table 4.

20

25

Table 4

| Ex. No. | Item   |  |
|---------|--|--|
|         | Negative Electrode-Active Material (average particle size: 20 $\mu$ m) | Binder Resin Composition (a solution in NMP)               |
| 6       | Artificial graphite  | The product of the present invention prepared in Example 1 |
| 7*      | Amorphous carbon   | PVDF   |
| 8*      | Artificial graphite  | PVDF   |
| 9*      | Amorphous carbon   | The component (A) alone prepared in Synthetic Example 1    |
| 10*     | Artificial graphite  | The component (A) alone prepared in Synthetic Example 1    |

\*: Comparative Example

Note 1: The volume ratio of the negative electrode-active material to the binder resin composition (solid contents) was identical to that used in Example 5.

#### Example 7 (Preparation of Positive Electrode)

The slurry of the positive electrode mix prepared in Example 2 was applied onto the both sides of a current collector (an aluminum foil) having a thickness of 20  $\mu$ m such that the coated amount of the slurry was 290 g/m<sup>2</sup> per side and then the coated layer was dried to give an electrode mix layer. Then the resulting product was rolled using a roller press machine such that the bulk density of the electrode mix was 2.6 g/cm<sup>3</sup>, followed by cutting the rolled product into strips each having a width of 54 mm to form electrode mix sheets in the form of tanzaku (a strip of fancy paper). After welding, under the application of ultrasonics, a collector tab of aluminum to an edge of each sheet, the resulting assembly was dried at 150°C for 16 hours in a vacuum for the removal of any volatile components such as the remaining solvents and the adsorbed moisture to thus give a positive electrode.

## Examples 8 and 9 and Comparative Examples 11 to 16 (Preparation of Positive Electrodes)

The same procedures used in Example 7 were repeated except for using slurries of positive electrode mixes detailed in the following Table 5 to thus produce corresponding positive electrodes.

Table 5

| Item         | Slurry of Positive Electrode Mix                           |
|--------------|--|
| Ex. 8        | The product of the present invention prepared in Example 3 |
| Ex. 9        | The product of the present invention prepared in Example 4 |
| Comp. Ex. 11 | The product prepared in Comparative Example 1              |
| Comp. Ex. 12 | The product prepared in Comparative Example 2              |
| Comp. Ex. 13 | The product prepared in Comparative Example 3              |
| Comp. Ex. 14 | The product prepared in Comparative Example 4              |
| Comp. Ex. 15 | The product prepared in Comparative Example 5              |
| Comp. Ex. 16 | The product prepared in Comparative Example 6              |

## Example 10 (Preparation of Negative Electrode)

The slurry of the negative electrode mix prepared in Example 5 was applied onto the both sides of a current collector (a copper foil) having a thickness of 10  $\mu$ m such that the coated amount of the slurry was 65 g/m<sup>2</sup> per side and then the coated layer was dried to give an electrode mix layer. Then the resulting product was rolled using a roller press machine such that the bulk density of the electrode mix was 1.0 g/cm<sup>3</sup>, followed by cutting the rolled product into strips each having a width of 56 mm to form electrode mix sheets in the form of tanzaku (a strip of fancy paper). After welding, under the application of ultrasonics, a collector tab of aluminum to an edge of each sheet, the resulting assembly was dried at 150°C for 16 hours in a vacuum



for the removal of any volatile components such as the remaining solvents and the adsorbed moisture to thus give a negative electrode.

5 Example 11 and Comparative Examples 17 to 20 (Preparation of Negative Electrodes)

The same procedures used in Example 10 were repeated except for using slurries of negative electrode mixes detailed in the following Table 6 to thus produce corresponding negative electrodes.

10 Table 6

| Item         | Slurry of Negative Electrode Mix                             |
|--------------|--|
| Ex. 11       | The product of the present invention prepared in Example 6   |
| Comp. Ex. 17 | The product of the present invention prepared in Comp. Ex. 7 |
| Comp. Ex. 18 | The product prepared in Comp. Ex. 8                          |
| Comp. Ex. 19 | The product prepared in Comp. Ex. 9                          |
| Comp. Ex. 20 | The product prepared in Comp. Ex. 10                         |

The resulting electrodes were inspected for the conditions (such as the presence of peeling and the presence of any crack) of the electrode mix (EM) layers and any change of the appearance observed after the immersion of  
15 these electrodes in a non-aqueous electrolysis solution. The results thus obtained are listed in the following Table 7.

Table 7

| Item                      | Conditions of EM Layer                | Change of Appearance*                             |
|---------------------------|---------------------------------------|---|
| Electrode of Ex. 7        | No peeling or crack                   | No change of appearance                           |
| Electrode of Ex. 8        | No peeling or crack                   | No change of appearance                           |
| Electrode of Ex. 9        | No peeling or crack                   | No change of appearance                           |
| Electrode of Ex. 10       | No peeling or crack                   | No change of appearance                           |
| Electrode of Ex. 11       | No peeling or crack                   | No change of appearance                           |
| Electrode of Comp. Ex. 11 | No peeling or crack                   | Swelling of superficial binder, surface coating** |
| Electrode of Comp. Ex. 12 | No peeling or crack                   | Swelling of superficial binder, surface coating   |
| Electrode of Comp. Ex. 13 | No peeling or crack                   | Swelling of superficial binder, surface coating   |
| Electrode of Comp. Ex. 14 | Peeled off and cracked after pressing | --  |
| Electrode of Comp. Ex. 15 | Peeled off and cracked after pressing | --  |
| Electrode of Comp. Ex. 16 | Peeled off and cracked after pressing | --  |
| Electrode of Comp. Ex. 17 | No peeling or crack                   | Swelling of superficial binder, surface coating   |
| Electrode of Comp. Ex. 18 | No peeling or crack                   | Swelling of superficial binder, surface coating   |
| Electrode of Comp. Ex. 19 | Peeled off and cracked after pressing | --  |
| Electrode of Comp. Ex. 20 | Peeled off and cracked after pressing | --  |

\*: Change of the appearance of an electrode observed after immersing in a non-aqueous electrolysis solution: After immersing the electrode in the electrolysis solution at 50°C for 24 hours, the appearance thereof was

5 observed under an electron microscope of 1000 magnifications.

\*\* : The term "surface coating" means that the binder covers the surface of the active material.

The results listed in Table 7 indicate that the electrodes prepared using PVDF (Comparative Examples) or only the component (A) cannot

10 simultaneously satisfy the requirements for the adherence, flexibility and

electrolysis solution resistance of the electrode mix layers, while the electrodes prepared using the thermosetting binder resin compositions of the present invention can simultaneously satisfy all of these requirements.

5    Examples 12 to 18 and Comparative Examples 21 to 23 (Preparation of Lithium Secondary Batteries)

10        The positive electrodes prepared in the foregoing Examples 7 to 9 and Comparative Examples 11 to 13 and the negative electrodes prepared in Examples 10 and 11 and Comparative Examples 17 and 18 were variously combined as specified in the following Table 8 and each pair of the electrodes was wound through microporous membrane separator of polyethylene having a thickness of 25  $\mu$ m and a width of 58 mm to form a series of spiral rolls. Each roll was inserted into a can for cell, the nickel tab terminal, which had been welded to the copper foil or the current collector for negative  
15    electrode in advance, was welded to the bottom of the can for cell and the aluminum tab terminal, which had been welded to the aluminum foil or the current collector for positive electrode in advance, was welded to a cap. Then 5 ml of a non-aqueous electrolysis solution (a 1M solution of lithium hexafluoro-phosphate in a 1/1/1 (volume ratio) mixed liquid of ethylene  
20    carbonate/dimethyl carbonate/diethyl carbonate) was introduced into the can for cell and then the can was caulked to tightly seal and to thus form a cylindrical lithium secondary battery having a diameter of 18 mm and a height of 65 mm.

25        The lithium secondary batteries prepared in Examples 12 to 14 and Comparative Example 21 were constant voltage-charged at a charging current of 400 mA and a limit voltage of 4.2 V and then discharged at a

discharge current of 800 mA till the voltage thereof reached the termination voltage of 2.7 V to thus determine the initial discharge capacities of these batteries.

In addition, the lithium secondary batteries prepared in Examples 15  
5 and 17 and Comparative Example 22 were constant voltage-charged at a charging current of 750 mA and a limit voltage of 4.2 V and then discharged at a discharge current of 1500 mA till the voltage thereof reached the termination voltage of 2.5 V to thus determine the initial discharge capacities of these batteries.

10 Moreover, the lithium secondary batteries prepared in Examples 16 and 18 and Comparative Example 23 were constant voltage-charged at a charging current of 900 mA and a limit voltage of 4.15 V and then discharged at a discharge current of 1800 mA till the voltage thereof reached the termination voltage of 3.0 V to thus determine the initial discharge  
15 capacities of these batteries.

The charge-discharge under these conditions was defined to be one cycle and such charge-discharge cycles were repeated at an ambient temperature of 50°C till the discharge capacity of the cell was reduced to a level of less than 70% of the initial discharge capacity (a criteria for judging  
20 whether the high temperature service life of a cell ran down or not) to thus determine the number of charge-discharge cycles. The results thus obtained are listed in the following Table 8.

Table 8

| Ex. No. | Item                    |                        |               |
|---------|-------------------------|------------------------|---------------|
|         | Positive Electrode      | Negative Electrode     | No. of Cycles |
| 12      | Ex. 7 (Mn, PVA)         | Ex. 10 (P, PVA)        | 300           |
| 13      | Ex. 7 (Mn, PVA)         | Comp. Ex. 17 (P, PVDF) | 250           |
| 14      | Comp. Ex. 11 (Mn, PVDF) | Ex. 10 (P, PVA)        | 280           |
| 15      | Ex. 8 (Co, PVA)         | Ex. 11 (G, PVA)        | 250           |
| 16      | Ex. 9 (Ni, PVA)         | Ex. 11 (G, PVA)        | 280           |
| 17      | Comp. Ex. 12 (Co, PVDF) | Ex. 11 (G, PVA)        | 250           |
| 18      | Comp. Ex. 13 (Ni, PVDF) | Ex. 11 (G, PVA)        | 250           |
| 21*     | Comp. Ex. 11 (Mn, PVDF) | Comp. Ex. 17 (P, PVDF) | 50            |
| 22*     | Comp. Ex. 12 (Co, PVDF) | Comp. Ex. 17 (P, PVDF) | 200           |
| 23*     | Comp. Ex. 13 (Ni, PVDF) | Comp. Ex. 18 (G, PVDF) | 150           |

\*: Comparative Example

Mn: this means that the positive electrode-active material is lithium-rich lithium manganese(III,IV) oxide.

5 Co: this means that the positive electrode-active material is lithium cobalt(III) oxide.

Ni: this means that the positive electrode-active material is lithium nickel(III) oxide.

10 P: this means that the negative electrode-active material is amorphous carbon.

G: this means that the negative electrode-active material is artificial graphite.

PVA: this means that the binder resin composition used is the product of Example 1 according to the present invention.

15 PVDF: this means that the binder resin composition used is PVDF.

The results listed in Table 8 indicate that the cell of Comparative Example 21 comprising a combination of a positive electrode prepared using

lithium-rich lithium manganese(III,IV) oxide as an active material and PVDF as a binder resin with a negative electrode comprising a combination of amorphous carbon as an active material and PVDF as a binder resin can repeatedly be charged and discharged only over 50 cycles till the service life  
5 of the cell ran down, while the lithium secondary batteries of Examples 12 to 14 according to the present invention in which the thermosetting binder resin composition of the present invention is used in at least one of positive and negative electrodes have an improved or extended service life on the order of not less than 250 cycles.

10 When the batteries whose service life ran down were taken to pieces, it was recognized that the negative electrode mix layer was peeled off from the copper foil as the current collector, among others, in the cell of Comparative Example 21 and there was observed deposition of metal lithium on that portion, while there were not observed such defects at all in the  
15 lithium secondary batteries of Examples 12 and 14.

From the foregoing, it can be confirmed that the lithium secondary battery, which makes use of the thermosetting binder resin composition of the present invention, is excellent in the electrolysis solution resistance at a high temperature (50°C) in the proximity to the upper limit of the cell-  
20 operating temperature, that good adherence at the boundary between the current collector and the electrode mix layers and between the active materials present in the electrode mix layers is ensured since the degree of swelling through the absorption of an electrolysis solution is considerably low and that the reduction of the discharge capacity of the cell is thus  
25 significantly retarded.

**Example 19 (Preparation of Thermosetting Polyvinyl Alcoholic Binder Resin)**

To a 0.5 liter volume separable flask equipped with a stirring machine, a thermometer, a condenser, a distillation tube and a nitrogen gas-introduction tube, there were added 24.2 g of a polyvinyl alcohol (available from Unitika Ltd. under the trade name of Unitika Poval UF200G, the average degree of polymerization: 2000; the degree of saponification: 98 to 99 mole%; the content of adsorbed water and others (weight loss observed after drying on a hot plate of 150°C for 30 minutes): 6.3% by mass), as a raw material, 322 g of N-methyl-2-pyrrolidone (NMP) as a solvent and 10 g of toluene as a solvent for azeotropic dehydration and the temperature was raised up to 190°C by heating over 30 minutes in a nitrogen gas stream with stirring. Moisture present in the system began to be distilled off in the form of an azeotropic mixture with toluene in the course of the heating and from an instance when the temperature exceeded about 180°C. The mixture was maintained at that temperature for 1 to 2 hours till all of the moisture was thus substantially distilled off from the system while refluxing the toluene, the toluene in the system was distilled off and then the system was cooled down to 120°C. The distillate (moisture and others) was found to be about 2 ml.

Then, to the dehydrated solution of the polyvinyl alcohol maintained at 120°C, there was added 2.75 g of dodecenyl succinic acid anhydride (available from WAKO Pure Chemical Co., Ltd., electron microscope grade, 0.02 equivalent as expressed in terms of the amount of the acid anhydride groups per one equivalent of the alcoholic hydroxyl groups of the polyvinyl alcohol), the mixture was maintained at that temperature for one hour to thus make the reaction proceed. Subsequently, 2.58 g of succinic acid

anhydride (0.05 equivalent as expressed in terms of the amount of the acid anhydride groups per one equivalent of the alcoholic hydroxyl groups of the polyvinyl alcohol) was added to the reaction system, the mixture was maintained at that temperature for one hour to thus make the reaction  
5 proceed and then cooled down to room temperature to give a thermosetting polyvinyl alcoholic binder resin (an NMP solution having a resin content of 8% by mass) according to the present invention.

The resulting product of the present invention was found to have a weight average molecular weight (as determined by GPC and more  
10 specifically, determined using, as an eluent, an aqueous solution prepared in such a manner that the concentration of sodium chloride as an emollient agent was 0.1 mole/l, and a calibration curve prepared using standard polyethylene oxide-polyethylene glycol, as expressed in terms of a polyethylene oxide-polyethylene glycol-reduced value) of 73,000 and an acid  
15 value of 78 KOH mg/g.

In addition, the SP value of the resulting thermosetting polyvinyl alcoholic binder resin was found to be  $25.3 \text{ (MJ/m}^3)^{1/2}$ .

The thermosetting properties and the electrolysis solution resistance  
20 of the product obtained in Example 19 were evaluated by comparing it with the polyvinyl alcohol as the raw material (Raw PVA) prepared in Preparation Example 1 and PVDF. The method for preparing a film and the methods for evaluating the thermosetting properties and the electrolysis solution resistance are identical to those described above. The following Table 9  
25 shows the results obtained in the evaluation of the thermosetting properties and the electrolysis solution resistance.



Table 9

| Item                             |                                | Product of the invention               | Raw PVA              | PVDF                 |
|----------------------------------|--------------------------------|--|----------------------|----------------------|
| Thermosetting Properties         | Dissolved Condition of Film    | Insoluble (keeping the original shape) | Completely dissolved | Completely dissolved |
|                                  | Judgment                       | good                                   | bad                  | bad                  |
| Electrolysis Solution Resistance | Degree of swelling at 25°C (%) | 1                                      | 9                    | 16                   |
|                                  | Degree of swelling at 50°C (%) | 2                                      | 4                    | 20                   |
|                                  | Judgment                       | good                                   | bad                  | acceptable           |

The foregoing results indicate that the thermosetting polyvinyl alcoholic binder resin carrying thermosetting units represented by Formula (III) possesses good thermosetting properties and good electrolysis solution resistance which can never be attained by polyvinyl alcohol as the raw material and PVDF.

#### Example 20 (Preparation of Slurry of Positive Electrode Mix)

There were admixed lithium-rich lithium manganese(III,IV) oxide ( $\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$ ), as a positive electrode-active material, having an average particle size of  $10\mu\text{m}$ , an auxiliary conductivity-imparting agent (artificial graphite) having an average particle size of  $3\mu\text{m}$  and the thermosetting polyvinyl alcoholic binder resin (an NMP solution having a resin content of 8% by mass) prepared in Example 19 in a volume ratio of 80 : 10 : 10 (solid contents), followed by kneading the mixture while NMP was, if necessary, supplemented to the mixture to prepare a slurry of positive electrode mix.

# Examples 21 and 22 and Comparative Examples 24 to 26 (Preparation of Slurries of Positive Electrode Mixes)

The same procedures used in Example 20 were repeated except for using components listed in the following Table 10 to thus give corresponding slurries of positive electrode mixes having compositions specified in Table 10.

Table 10

| Ex. No. | Item   |  |
|---------|--|--|
|         | Positive electrode-active material (average particle size: 10 $\mu$ m) | Binder Resin (Solution in NMP)         |
| 21      | Lithium cobalt(III) oxide  | The product of Ex. 19 of the invention |
| 22      | Lithium nickel(III) oxide  | The product of Ex. 19 of the invention |
| 24*     | Lithium-rich lithium manganese(III,IV) oxide                           | PVDF                                   |
| 25*     | Lithium cobalt(III) oxide  | PVDF                                   |
| 26*     | Lithium nickel(III) oxide  | PVDF                                   |

\*: Comparative Example

Note 1: The auxiliary conductivity-imparting agent used is identical to that used in Example 20.

Note 2: The relative volume rate of the positive electrode-active material, the auxiliary conductivity-imparting agent and the binder resin (solid contents) is likewise identical to that used in Example 20.

## Example 23 (Preparation of Slurries of Negative Electrode Mixes)

There were admixed amorphous carbon having an average particle size of 20  $\mu$ m as a negative electrode-active material and the thermosetting polyvinyl alcoholic binder resin (an NMP solution having a resin content of 8% by mass) prepared in Example 19 in a volume ratio (of solid contents) of

90 : 10, followed by kneading the mixture while NMP was, if necessary, supplemented to prepare a slurry of negative electrode mix.

#### Example 24 and Comparative Examples 27 to 29 (Preparation of Slurries of Negative Electrode Mixes)

The same procedures used in Example 23 were repeated except for using components listed in the following Table 11 to thus give corresponding slurries of negative electrode mixes having compositions specified in Table 11.

Table 11

| Ex. No. | Item  |   |
|---------|---|---|
|         | Negative Electrode-Active Material (average particle size: 10 $\mu\text{m}$ ) | Binder Resin Composition (a solution in NMP)                        |
| 24      | Artificial graphite   | The product of the present invention prepared in Example 19         |
| 27*     | Amorphous carbon  | PVDF  |
| 28*     | Artificial graphite   | PVDF  |
| 29*     | Artificial graphite   | The raw polyvinyl alcohol prepared in Synthetic Example 1(aq. sol.) |

\*: Comparative Example

Note 1: The volume ratio of the negative electrode-active material to the binder resin (solid contents) was identical to that used in Example 23.

#### Example 25 (Preparation of Positive Electrode)

The slurry of the positive electrode mix prepared in Example 20 was applied onto the both sides of a current collector (an aluminum foil) having a thickness of 20  $\mu\text{m}$  such that the coated amount of the slurry was 290  $\text{g/m}^2$  per side and then the coated layer was dried to give an electrode mix layer.

Then the resulting product was rolled using a roller press machine such that the bulk density of the electrode mix was 2.6 g/cm<sup>3</sup>, followed by cutting the rolled product into strips each having a width of 54 mm to form electrode mix sheets in the form of tanzaku (a strip of fancy paper). After welding, under the application of ultrasonics, a collector tab of aluminum to an edge of each sheet, the resulting assembly was dried at 150°C for 16 hours in a vacuum for the removal of any volatile components such as the remaining solvents and the adsorbed moisture to thus give a positive electrode.

#### 10 Examples 26 and 27 and Comparative Examples 30 to 32 (Preparation of Positive Electrodes)

The same procedures used in Example 25 were repeated except for using slurries of positive electrode mixes detailed in the following Table 12 to thus produce corresponding positive electrodes.

15

Table 12

| Item         | Slurry of Positive Electrode Mix                    |
|--------------|---|
| Ex. 26       | The product of the invention prepared in Example 21 |
| Ex. 27       | The product of the invention prepared in Example 22 |
| Comp. Ex. 30 | The product prepared in Comparative Example 24      |
| Comp. Ex. 31 | The product prepared in Comparative Example 25      |
| Comp. Ex. 32 | The product prepared in Comparative Example 26      |

#### Example 28 (Preparation of Negative Electrode)

The slurry of the negative electrode mix prepared in Example 23 was applied onto the both sides of a current collector (a copper foil) having a thickness of 10 μm such that the coated amount of the slurry was 65 g/m<sup>2</sup> per side and then the coated layer was dried to give an electrode mix layer. Then

the resulting product was rolled using a roller press machine such that the bulk density of the electrode mix was 1.0 g/cm<sup>3</sup>, followed by cutting the rolled product into strips each having a width of 56 mm to form electrode mix sheets in the form of tanzaku (a strip of fancy paper). After welding, under the application of ultrasonics, a collector tab of aluminum to an edge of each sheet, the resulting assembly was dried at 150°C for 16 hours in a vacuum for the removal of any volatile components such as the remaining solvents and the adsorbed moisture to thus give a negative electrode.

#### 10. Example 29 and Comparative Examples 33 to 35 (Preparation of Negative Electrodes)

The same procedures used in Example 28 were repeated except for using slurries of negative electrode mixes detailed in the following Table 13 to thus produce corresponding negative electrodes.

Table 13

| Item         | Slurry of Negative Electrode Mix                    |
|--------------|---|
| Ex. 29       | The product of the invention prepared in Example 24 |
| Comp. Ex. 33 | The product prepared in Comp. Ex. 27                |
| Comp. Ex. 34 | The product prepared in Comp. Ex. 28                |
| Comp. Ex. 35 | The product prepared in Comp. Ex. 29                |

The resulting electrodes were inspected for the conditions (such as the presence of peeling, the presence of any crack) of the electrode mix (EM) layers and any change of the appearance observed after the immersion of these electrodes in a non-aqueous electrolysis solution. The results thus obtained are listed in the following Table 14.

Table 14

| Item                         | Conditions of EM Layer                   | Change of Appearance*                              |
|------------------------------|--|--|
| Electrode of Ex. 25          | No peeling or crack                      | No change of appearance                            |
| Electrode of Ex. 26          | No peeling or crack                      | No change of appearance                            |
| Electrode of Ex. 27          | No peeling or crack                      | No change of appearance                            |
| Electrode of Ex. 28          | No peeling or crack                      | No change of appearance                            |
| Electrode of Ex. 29          | No peeling or crack                      | No change of appearance                            |
| Electrode of<br>Comp. Ex. 30 | No peeling or crack                      | Swelling of superficial<br>binder, surface coating |
| Electrode of<br>Comp. Ex. 31 | No peeling or crack                      | Swelling of superficial<br>binder, surface coating |
| Electrode of<br>Comp. Ex. 32 | No peeling or crack                      | Swelling of superficial<br>binder, surface coating |
| Electrode of<br>Comp. Ex. 33 | No peeling or crack                      | Swelling of superficial<br>binder, surface coating |
| Electrode of<br>Comp. Ex. 34 | No peeling or crack                      | Swelling of superficial<br>binder, surface coating |
| Electrode of<br>Comp. Ex. 35 | Peeled off and cracked<br>after pressing | --   |

\*: Change of the appearance of an electrode observed after immersing in a non-aqueous electrolysis solution: After immersing the electrode in the electrolysis solution at 50°C for 24 hours, the appearance thereof was observed under an electron microscope of 1000 magnifications.

The above results indicate that the electrodes prepared using PVDF (Comparative Examples) or the polyvinyl alcohol as the raw material cannot simultaneously satisfy the requirements for the adherence, flexibility and electrolysis solution resistance of the electrode mix layers, while the electrodes prepared using the thermosetting polyvinyl alcoholic binder resin of the present invention can simultaneously satisfy all of these requirements.

Examples 30 to 36 and Comparative Examples 36 to 38 (Preparation of Lithium Secondary Batteries)

The positive electrodes prepared in the foregoing Examples 25 to 27 and Comparative Examples 30 to 32 and the negative electrodes prepared in Examples 28 and 29 and Comparative Examples 33 and 34 were variously combined as specified in the following Table 15 and each pair of the electrodes was wound through microporous membrane separator of polyethylene having a thickness of 25  $\mu$ m and a width of 58 mm to form a series of spiral rolls. Each roll was inserted into a can for cell, the nickel tab terminal, which had been welded to the copper foil or the current collector for negative electrode in advance, was welded to the bottom of the can for cell and the aluminum tab terminal, which had been welded to the aluminum foil or the current collector for positive electrode in advance, was welded to a cap. Then 5 ml of a non-aqueous electrolysis solution (a 1M solution of lithium hexafluoro-phosphate in a 1/1/1 (volume ratio) mixed liquid of ethylene carbonate/dimethyl carbonate/diethyl carbonate) was introduced into the can and then the can was caulked to tightly seal and to thus form a cylindrical lithium secondary battery having a diameter of 18 mm and a height of 65 mm.

The lithium secondary batteries prepared in Examples 30 to 32 and Comparative Example 36 were constant voltage-charged at a charging current of 400 mA and a limit voltage of 4.2 V and then discharged at a discharge current of 800 mA till the voltage thereof reached the termination voltage of 2.7 V to thus determine the initial discharge capacities of these batteries.

In addition, the lithium secondary batteries prepared in Examples 33 and 35 and Comparative Example 37 were constant voltage-charged at a charging current of 750 mA and a limit voltage of 4.2 V and then discharged

at a discharge current of 1500 mA till the voltage thereof reached the termination voltage of 2.5 V to thus determine the initial discharge capacities of these batteries.

Moreover, the lithium secondary batteries prepared in Examples 34 and 36 and Comparative Example 38 were constant voltage-charged at a charging current of 900 mA and a limit voltage of 4.15 V and then discharged at a discharge current of 1800 mA till the voltage thereof reached the termination voltage of 3.0 V to thus determine the initial discharge capacities of these batteries.

The charge-discharge under these conditions was defined to be one cycle and such charge-discharge cycles were repeated at an ambient temperature of 50°C till the discharge capacity of the cell was reduced to a level of less than 70% of the initial discharge capacity (a criteria for judging whether the high temperature service life of a cell ran down or not) to thus determine the number of charge-discharge cycles. The results thus obtained are listed in the following Table 15.

Table 15

| Ex. No. | Item                    |                        |               |
|---------|-------------------------|------------------------|---------------|
|         | Positive Electrode      | Negative Electrode     | No. of Cycles |
| 30      | Ex. 25 (Mn, PVA)        | Ex. 28 (P, PVA)        | 300           |
| 31      | Ex. 25 (Mn, PVA)        | Comp. Ex. 33 (P, PVDF) | 250           |
| 32      | Comp. Ex. 30 (Mn, PVDF) | Ex. 28 (P, PVA)        | 280           |
| 33      | Ex. 26 (Co, PVA)        | Ex. 29 (G, PVA)        | 250           |
| 34      | Ex. 27 (Ni, PVA)        | Ex. 29 (G, PVA)        | 280           |
| 35      | Comp. Ex. 31 (Co, PVDF) | Ex. 29 (G, PVA)        | 250           |
| 36      | Comp. Ex. 32 (Ni, PVDF) | Ex. 29 (G, PVA)        | 250           |
| 36*     | Comp. Ex. 30 (Mn, PVDF) | Comp. Ex. 33 (P, PVDF) | 50            |
| 37*     | Comp. Ex. 31 (Co, PVDF) | Comp. Ex. 33 (P, PVDF) | 200           |
| 38*     | Comp. Ex. 32 (Ni, PVDF) | Comp. Ex. 34 (G, PVDF) | 150           |



\*: Comparative Example

Mn: this means that the positive electrode-active material is lithium-rich lithium manganese(III,IV) oxide.

Co: this means that the positive electrode-active material is lithium  
5 cobalt(III) oxide.

Ni: this means that the positive electrode-active material is lithium nickel(III) oxide.

P: this means that the negative electrode-active material is amorphous carbon.

10 G: this means that the negative electrode-active material is artificial graphite.

PVA: this means that the binder resin used is the product of Example 19 according to the present invention.

PVDF: this means that the binder resin used is PVDF.

15

The results listed in Table 15 indicate that the cell of Comparative Example 36 comprising a combination of a positive electrode prepared using lithium-rich lithium manganese(III,IV) oxide as an active material and PVDF as a binder resin with a negative electrode comprising a combination  
20 of amorphous carbon as an active material and PVDF as a binder resin can repeatedly be charged and discharged only over 50 cycles till the service life of the cell ran down, while the lithium secondary batteries of Examples 30 to 32 according to the present invention in which the thermosetting polyvinyl alcoholic binder resin of the present invention is used in at least one of  
25 positive and negative electrodes have an improved or extended service life on the order of not less than 250 cycles.

When the batteries whose service life ran down were taken to pieces, it was recognized that the negative electrode mix layer was peeled off from the copper foil as the current collector among others in the cell of Comparative Example 36 and there was observed deposition of metal lithium on that portion, while there were not observed such defects at all in the lithium secondary batteries of Examples 30 and 32.

From the foregoing, it has been confirmed that the lithium secondary battery, which makes use of the thermosetting polyvinyl alcoholic binder resin of the present invention, is excellent in the electrolysis solution resistance at a high temperature (50°C) in the proximity to the upper limit of the cell-operating temperature, that good adherence at the boundary between the current collector and the electrode mix layers and between the active materials present in the electrode mix layers is ensured since the degree of swelling through the absorption of an electrolysis solution is considerably low and that the reduction of the discharge capacity of the cell is thus significantly retarded.

#### Industrial Applicability

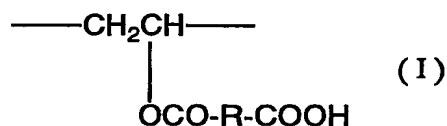
The present invention provides a thermosetting polyvinyl alcoholic binder resin, which is excellent in the electrolysis solution resistance at a high temperature (50°C) in the proximity to the upper limit of the cell-operating temperature of the lithium secondary battery, which never causes any cracking, peeling off and dropping out of the electrode mix layer containing the same during the preparation of batteries and which has good softness and flexibility. Moreover, the use of electrodes prepared from slurries of electrode mixes containing the thermosetting polyvinyl alcoholic

binder resin permits the production of a non-aqueous electrolysis solution-containing secondary battery, whose reduction of the energy capacity in the charge-discharge cycles at 50°C can significantly be retarded and whose service life can substantially be extended, as compared with the conventional  
5 batteries produced using PVDF as a binder resin.

# Claims

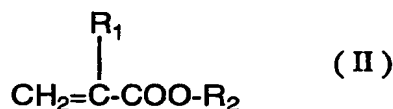
1. A thermosetting binder resin composition which comprises (A) a thermosetting polyvinyl alcoholic binder resin, (B) an acrylic resin plasticizer  
5 and (C) a solvent.

2. The thermosetting binder resin composition of claim 1, wherein the component (A) has thermosetting units represented by the following general formula (I):



wherein R represents a divalent organic group.

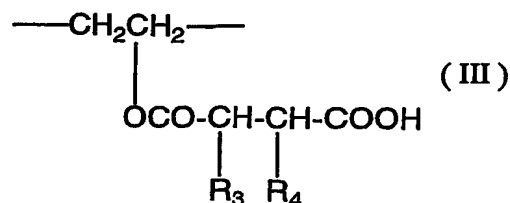
10 3. The thermosetting binder resin composition of claim 1, wherein the component (B) is a polymerized product derived from a monomer represented by the following general formula (II):



wherein R<sub>1</sub> represents a hydrogen atom or a methyl group and R<sub>2</sub> represents a hydrogen atom, a glycidyl group or an alkyl group having 6 to 18 carbon  
15 atoms, or a derivative thereof.

4. The thermosetting binder resin composition as set forth in any one of claims 1 to 3, wherein the component (C) is a nitrogen atom-containing organic solvent or a mixed solvent containing the same.

5. A thermosetting binder resin composition which comprises a  
20 thermosetting polyvinyl alcoholic binder resin having thermosetting units represented by the following general formula (III):



wherein one of  $\text{R}_3$  and  $\text{R}_4$  represents a hydrogen atom and the other represents an alkenyl group, and a solvent.

6. The thermosetting binder resin composition of claim 5, wherein the alkenyl group in the thermosetting unit is a dodecenyl group.

5 7. A thermosetting binder resin composition which comprises a thermosetting binder resin whose solubility parameter ranges from 24.5 to 26.5  $(\text{MJ/m}^3)^{1/2}$  and a solvent.

8. A slurry of an electrode mix which comprises a thermosetting binder resin composition as set forth in any one of claims 1 to 7 and a positive or  
10 negative electrode-active material.

9. The slurry of an electrode mix of claim 8, wherein the positive electrode-active material is a lithium-containing metal compound oxide capable of reversibly inserting and releasing lithium ions by charge-discharge cycles.

15 10. The slurry of an electrode mix of claim 8, wherein the negative electrode-active material is a carbonaceous material capable of reversibly inserting and releasing lithium ions by charge-discharge cycles.

11. An electrode characterized in that it is prepared by applying the slurry of an electrode mix as set forth in any one of claims 8 to 10 onto a  
20 current collector and then drying the coated layer of the slurry.

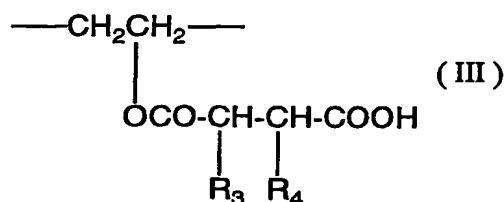
12. A non-aqueous electrolysis solution-containing secondary battery which comprises the electrode as set forth in claim 11.

13. A non-aqueous electrolysis solution-containing secondary battery which comprises electrodes and an electrolysis solution containing a chain organic solvent, wherein the electrode is one prepared by applying a slurry of an electrode mix, which comprises a thermosetting binder resin composition  
 5 and a positive or negative electrode-active material, onto a current collector and then drying the coated slurry and wherein the difference between the solubility parameter (SP value) of the thermosetting binder resin and the SP value of the chain organic solvent is not less than  $3 \text{ (MJ/m}^3)^{1/2}$ .

14. The non-aqueous electrolysis solution-containing secondary battery  
 10 of claim 13, wherein the degree of swelling, as determined at  $50^\circ\text{C}$ , of the thermosetting binder resin with respect to the electrolysis solution is not smaller than that as determined at  $25^\circ\text{C}$  and the former is less than 10%.

15. The non-aqueous electrolysis solution-containing secondary battery of claim 13, wherein the thermosetting binder resin has a winding ability.

16. The non-aqueous electrolysis solution-containing secondary battery  
 15 of claim 13, wherein the thermosetting binder resin is a thermosetting polyvinyl alcoholic binder resin having thermosetting units represented by the following general formula (III):



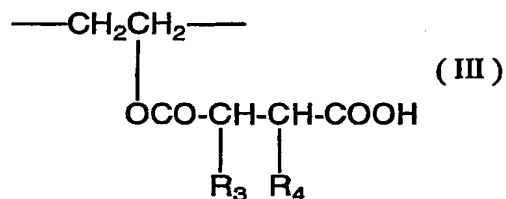
wherein one of  $\text{R}_3$  and  $\text{R}_4$  represents a hydrogen atom and the other  
 20 represents an alkenyl group.

17. The non-aqueous electrolysis solution-containing secondary battery of claim 16, wherein the alkenyl group present in the thermosetting unit is a

dodecenyl group.

18. The non-aqueous electrolysis solution-containing secondary battery of claim 13, wherein the thermosetting binder resin composition comprises (A) a thermosetting polyvinyl alcoholic binder resin, (B) an acrylic resin plasticizer and (C) a solvent.

19. A thermosetting polyvinyl alcoholic binder resin used as an electrode material for non-aqueous electrolysis solution-containing secondary batteries, which comprises thermosetting units represented by the following general formula (III):



20. wherein one of  $\text{R}_3$  and  $\text{R}_4$  represents a hydrogen atom and the other represents an alkenyl group.

20. The thermosetting polyvinyl alcoholic binder resin of claim 19, wherein the alkenyl group present in the thermosetting unit is a dodecenyl group.